Spectrochimica Acta Part B 101 (2014) 183–190

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Sensitive detection of chlorine in iron oxide by single pulse and dual pulse laser-induced breakdown spectroscopy☆

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ARTICLE INFO

Article history:
Received 20 December 2013
Accepted 8 August 2014
Available online 29 August 2014

Keywords:
Laser induced breakdown spectroscopy (LIBS)
Double-pulse excitation
Plasma absorption
Chlorine
Iron oxide

ABSTRACT

The halogen chlorine is hard to detect in laser-induced breakdown spectroscopy (LIBS) mainly due to its high excited state energies of 9.2 and 10.4 eV for the most intense emission lines at 134.72 nm and 837.59 nm, respectively. We report on sensitive detection of Cl in industrial iron oxide Fe_2O_3 powder by single-pulse (SP) and dual-pulse (DP) LIBS measurements in the near infrared range in air. In compacted powder measured by SP excitation (Nd:YAG laser, 532 nm) Cl was detected with limit of detection LOD = 440 ppm and limit of quantitation LOQ = 720 ppm. Orthogonal DP LIBS was studied on pressed Fe_2O_3 pellets and Fe_3O_4 ceramics. The transmission of laser-induced plasma for orthogonal Nd:YAG 1064 nm and ArF 193 nm laser pulses showed a significant dependence on interpulse delay time (ipd) and laser wavelength (λ_L). The UV pulses ($\lambda_L = 193$ nm) were moderately absorbed in the plasma and the Cl I emission line intensity was enhanced while IR pulses ($\lambda_L = 1064$ nm) were not absorbed and Cl signals were not enhanced at ipd = 3 μs. The UV laser enhancement of Cl signals is attributed to the much higher signal/background ratio for orthogonal DP excitation compared to SP excitation and to the increased plasma temperature and electron number density. This enabled measurement at a very short delay time of $t_d \geq 0.1$ μs with respect to the re-excitation pulse and detection of the very rapidly decaying Cl emission with higher efficiency.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a versatile element analytical technique that basically enables detection of all chemical elements in many different types of material (solids, liquids, gases, particulate matter) [1–4]. The reported limits of detection (LOD) for many elements are in the range of 1–30 ppm, typically. The unique strength of LIBS is its applicability to field measurements under harsh conditions [5–9]. Chlorine and Cl containing substances are used in many materials, e.g. various chemicals, disinfectants, food and nutrients (NaCl), pharmaceuticals, polymers (polyvinylchloride PVC), and solvents [10]. Some important applications are in the fabrication of consumer products, the production of concrete, polymers, silicon chips, and other technical materials, and in the purification of water. The reported LOD values for the LIBS measurement of Cl in concrete [11–15], soil [16], organic material [17–19], pharmaceutical substances [20], and layered material on steel [21] are summarized in Table 1. Depending on the type of solid matrix, the use of single (SP) or dual (DP) laser pulses for LIBS measurements, and other experimental parameters, the achieved LOD values range from a few percent to less than 0.1 wt.%. In concrete matrix, clear Cl signals have been detected at a concentration of 290 ppm (0.65 kg/m^3 [14]) and the lowest LOD values reported are 400 ppm (0.04 wt.%) for DP LIBS measurement [15] and 500 ppm for SP LIBS combined with a pulsed electric discharge [13]. The high detection limits for chlorine are in part due to the high excited state energy $E_k = 10.4$ eV for the most intense emission line in the UV–VIS–NIR range (at 837.59 nm). Other intense emission lines of Cl require vacuum-UV detection and are therefore difficult to measure. With DP LIBS higher sensitivity has been observed for many elements in complex matrices [22–24].

In this study, we present single-pulse (SP) and dual-pulse (DP) LIBS measurements of Cl in Fe_2O_3 powder from industrial steel processing. Compacted powder, pressed pellets, and sintered ceramics are investigated and Cl calibration curves are measured by SP LIBS. In order to evaluate DP excitation for enhancement of Cl signals we measure the absorption of orthogonal laser pulses in plasma and the DP LIBS spectra.

☆ Selected paper from the 7th Euro-Mediterranean Symposium on Laser Induced Breakdown Spectroscopy (EMSLIBS 2013), Bari, Italy, 16–20 September 2013.

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http://dx.doi.org/10.1016/j.sab.2014.08.028

The temporal evolution of Cl and Fe emission line intensities is recorded using UV laser pulses for re-excitation and the measured intensities are compared to calculated intensity profiles.

Table 1
Reported detection of chlorine in solid matrix materials by single-pulse (SP) and dual-pulse (DP) LIBS.Combination of LIBS and pulsed electric discharge (PED) in reference [13].

Material	Method	Ambient	λ (nm)	Detection	Ref.
Concrete	SP, DP	He	134.7	0.1 wt.%	[11]
	SP, DP	Air	594.8, 837.6	0.2 wt.%	[12]
	SP+PED	Air	837.6	0.05 wt.%	[13]
	SP, DP	He	837.6	290 ppm	[14]
	DP	Air	837.6	400 ppm	[15]
Soil	SP	CO_2	133.57	7.5 wt.%	[16]
Organic	SP	He	837.6	0.375 wt.%	[17]
	SP	Air, He	837.6	1.1 mol% (air), 0.09 mol% (He)	[18]
	SP	Vac.	134.7	5.4% Cl/C at. ratio	[19]
Pharmaceutical	SP	Air, He	837.6	0.29 wt.%	[20]
Layer on steel	SP, DP	Air	837.6	0.1 g/m^2	[21]

2. Experimental

2.1. Experimental setups

Two different series of LIBS measurements have been performed. In the first series, laser pulses of a Nd:YAG laser (Quantel CFR 200, ICE 450, wavelength $\lambda = 532$ nm, pulse duration 6 ns, pulse energy $E = 130$ mJ, pulse repetition rate $f_r = 15$ Hz) were focused on the surface of the iron oxide sample material (Fig. 1). The spot area and the laser fluence at the sample were $A_s = 0.5$ mm^2 and $\Phi = 26$ J/cm^2, respectively. The optical radiation of the laser-induced plasma was collected by a lens (focal length 50 mm) and imaged on the entrance face of a quartz fiber (core diameter 400 μm). An interference transmission filter with central wavelength $\lambda_0 = 839$ nm and full-width-at-half-maximum (FWHM) of 10 nm was used to block light at wavelengths far outside the spectral region of interest for Cl detection at 837.59 nm. A Czerny–Turner grating spectrometer (SpectraPro-500i, Acton Research Corporation, grating 1200 g mm^{-1}) covering the spectral range of 828–861 nm and a linear photodiode array (PDA, 1024 diodes) with a multichannel plate intensifier were used for recording the emission spectra. The delay time and gate width of the detection system were $t_d = 1.3$ μs and $t_g = 7$ μs, respectively. With these parameter values the measured emission intensity of Cl was relatively high and well above the background intensity. Measurements were performed in air and dust particles of ablated material were removed from the optical beam paths by an air suction system. The plasma emission was accumulated over 75 laser pulses (measurement time 5 s) on the detector and the spectrum was read out afterwards.

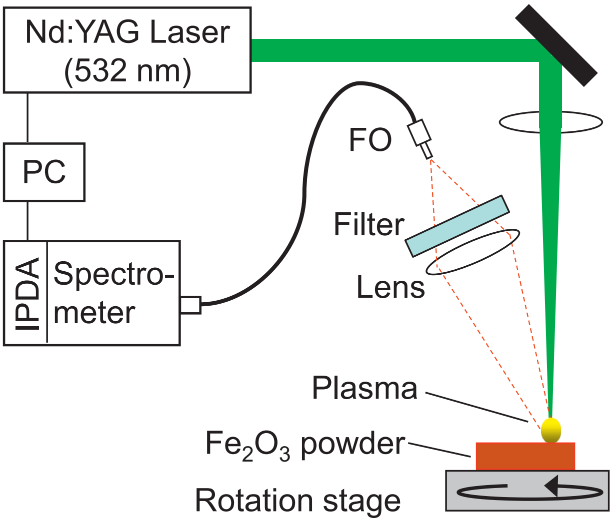

Fig. 1. Schematic setup for single-pulse LIBS measurement of iron oxide powder. The Fe_2O_3 is attached to a stage and ablated by single pulses of a frequency doubled Nd:YAG laser. Plasma emission is measured in air by using fiber optics (FO), Czerny–Turner spectrometer and intensified photo diode array (IPDA).

In the second series of experiments two time delayed laser pulses from different sources were applied to ablate the sample material and to re-excite the plasma induced by the first pulse. For ablation, the beam of a Nd:YAG laser (Quantel, Brilliant, $\lambda = 1064$ nm, $t_L = 6$ ns, $E_L = 140$ mJ, $A_s = 2.5$ mm^2, $\Phi = 5.5$ J/cm^2, $f_r = 10$ Hz) was expanded three-fold and focused with a 300 mm plano-convex lens onto the sample surface (Fig. 2). The re-excitation of plasma was performed in orthogonal geometry by applying pulses of a Nd:YAG laser (Litron, $\lambda = 1064$ nm, $t_L = 8$ ns, $E_L = 80$ mJ) or an ArF excimer laser (LambdaPhysik COMPexPro 102F, $\lambda = 193$ nm, $t_L = 15$ ns, $E_L = 80$ mJ). The second laser beams were focused into the plasma. The orthogonal Nd:YAG laser beam had a circular beam profile with a spot diameter of 1.2 mm in the focal plane ($\Phi = 7.1$ J/cm^2). The orthogonal ArF laser beam produced a rectangular shaped focal spot (0.8 mm × 2.8 mm) with the long axis oriented parallel to the sample surface ($\Phi = 3.6$ J/cm^2). For both types of second laser beams the fluence in the spot was not sufficient to achieve breakdown in clean air (i.e. without aerosols from ablation). The beam paths of orthogonal lasers were carefully adjusted to achieve maximum spatial overlap with the plasma and to avoid direct irradiation of the solid sample material. A ventilator was used to remove ablated particles from the optical beam paths by air flow. The LIBS spectra were measured using quartz fibers (F_1, F_2) and an Echelle spectrometer with intensified CCD (ICCD) camera (MultiChannel Instruments, Mechelle 7500, range 180–850 nm, spectral resolution $\lambda/\Delta\lambda = 3000$ at 850 nm) and the same Czerny–Turner spectrometer as used in the single pulse experiments. The coupling of plasma radiation into fibers was done without focusing lenses to avoid the effects of chromatic lens aberration (relevant especially for the broadband LIBS spectra). The interpulse delay time between the first and the second pulses, ipd = 0.1–15 μs, was set by a delay generator (Quantum composers, model 9614+, resolution 10 ns). The measurement setup was triggered by the ablation laser. The gating of spectrometers was varied to study the temporal evolution of plasma emission. Spectra were accumulated at the detector over several laser pulses and the emission lines were identified using atomic spectra databases [25,26]. For the calculation of plasma temperature T_e, broadband LIBS spectra measured with the Mechelle spectrometer were de-convolved using spectrometer transmission functions that were measured with the same setup. For plasma imaging a fast ICCD camera (Photometrics, ICCD S300:7895, 512 × 512 pixel, 14 bit) with a 105 mm objective lens (f/2.8 AF Micro Nikkon) was employed. The ICCD camera was mounted with its optical axis oriented parallel to the sample surface. For absorption measurement of the second laser pulses in the plasma, the pulse energies of either laser beam were recorded with two energy meters (E_1 and E_2 in Fig. 2).

2.2. Sample materials

Fe_2O_3 iron oxide powder from industrial production at voestalpine Stahl GmbH (Austria) was used as samples. The powder is formed by descaling of steel in hydrochloric pickling liquid. The powder consists of nano-particles that form micrometer-sized clusters which can agglomerate to larger granules [27]. The Fe_2O_3 phase represents approximately 99 wt.% of the powder mass. The nominal concentration of Cl in the samples investigated was in the range of 0.1–0.4 wt.% (1000–4000 ppm) as measured by wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF). The mass density of loose Fe_2O_3 powders was in the range of $\rho = 0.3$–0.8 g cm^{-3}, typically. For SP LIBS measurements the powder was slightly compacted ($\rho = 1.0$–1.2 g cm^{-3}) to